Solid-Liquid Equilibrium of Hard Dumbbells with Dipoles and Quadrupoles: Application to Methyl Chloride

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We calculate the solid-liquid equilibrium of a system of hard dumbbells with embedded point dipoles and quadrupoles in a generalized van der Waals theory. This work is an extension of earlier calculations for the purely dipolar system. The molecular parameters are chosen to approximate a system of methyl chloride molecules. The solid free energy is calculated by using the simple cell theory of Lennard-Jones and Devonshire to approximate the free energy of the hard-dumbbell solid with the multipole contributions to the free energy approximated by static lattice sums of the pair interactions. Two different crystal structures are considered as candidates for the structure of the solid at freezing, one of which is close packing. Thermodynamic perturbation theory is used to add dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions to the equation of state of the hard-dumbbell fluid. For the hard-dumbbell equation of state, we use that of Maeso and Solana. We carry out new Monte Carlo simulations to characterize the accuracy of the perturbation theory. Application of the Maxwell double-tangent construction yields the phase equilibrium between the solid and liquid. We are able to calculate the effect of molecular dipole and quadrupole moments on the phase diagram of the system of dumbbells. In particular, we examine the effects of the multipoles on the stable crystal structure at freezing, the ratio of triple point temperature to critical point temperature, and the density change at freezing.